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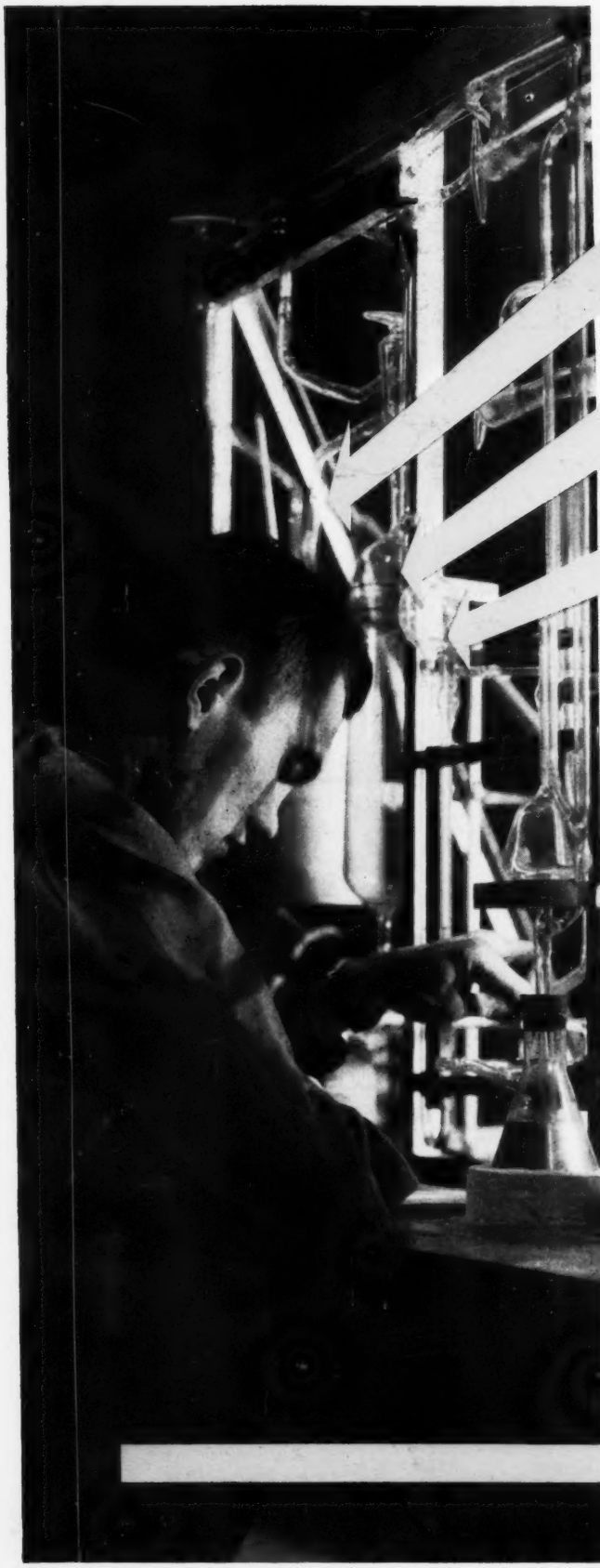

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VOLUME 28 OCTOBER 16, 1939 NUMBER 21

The Phthalocyanines

*A New Class of Synthetic Pigments and Dyes**

MILES A. DAHLEN**

The phthalocyanines are blue-to-green pigments and dyes containing the first new chromophore of commercial importance developed in a quarter of a century. Although closely related structurally to chlorophyll and hemin, there is no evidence that they occur in nature. The chemical and industrial history and scope of the development are reviewed.

Copper phthalocyanine, a brilliant blue pigment of excellent fastness properties and high tinctorial strength, is replacing the iron blues, ultramarine, and basic color lakes in the coloring of printing inks, paints, lacquers, rubber, wallpaper, linoleum, etc., especially in light and medium shades where the older colors lack the required fastness. Highly chlorinated copper phthalocyanine is a brilliant green of similar fastness which is replacing chrome greens, Pigment Green B, chromium tetrahydroxide and basic colors in the same applications. Metal-free phthalocyanine, intermediate in shade and similar in other properties, is being used in the same fields.

Sulfonated copper phthalocyanine is a brilliant greenish blue soluble dye of relatively low affinity for textile fibers and moderate fastness properties, used for paper coloring, mordant and direct dyeing of cotton, and in color mixtures for union fabrics. Its amine salts, soluble in spirit media, are used for the coloring of leather, wood stains, and similar materials. Insoluble toners and lakes of the sulfonated pigment have fastness properties approaching those of copper phthalocyanine itself and are finding similar uses.

The development is far from being a closed book, either scientifically or industrially, and it is possible that other additions to the ever-broadening line of pigments and dyes will come from this series.

THE history of the development of the methods and theories of organic chemistry is inseparable from the history of the synthetic dye industry. Most of the fundamental chemistry of aromatic compounds was developed in the half century following Perkin's discovery of mauve in 1856, and during the same half century all the important classes of dyes were discovered and attained commercial importance. The quarter century preceding 1927 was characterized by continued intensive research on synthetic dyes, but the important results were all in the nature of improvement of old colors or development of new colors of the types already known; no new chromophore of any importance in the dye industry was discovered in this period.

Investigation of the chemistry of natural products has been a major activity of academic research in organic chemistry in recent years. Recent researches have shown that the coloring matters of chlorophyll and the hemin group contain a new chromophore, and the new pigments and dyes which are the subject of this paper are closely related structurally to these natural coloring matters. It might have been assumed that the dye industry had obtained another valuable chromophore from these academic studies, but such is not the case. The academic studies were most valuable in determining the nature of the new colors described here, but their discovery was entirely independent.

In 1927 de Diesbach and von der Weid[10] described new insoluble blue compounds which they believed to be complex metal salts of aromatic *o*-dinitriles with copper and pyridine. By the action of cuprous cyanide, *o*-dibromobenzene, and pyridine, they obtained a blue insoluble compound to which they ascribed the formula $[C_6H_4(CN)_2 + C_5H_5N]_2Cu$. Undoubtedly this product was copper phthalocyanine. Their error in determining the nature of their products was probably due to the analytical difficulties characteristic of compounds of this series, coupled with the interest in metal complexes which had inspired their investigation. The following year Dandridge, Drescher, and Thomas[7] filed a patent application in Great Britain describing new insoluble colored organic compounds obtained by the action of ammonia on phthalic anhydride, phthalamide, or phthalimide in the presence of metals. They offered no theories as to the structure of these compounds, and did not recognize their identity with the products of de Diesbach and von der Weid. Nevertheless the first application of Dandridge, Drescher, and Thomas described the preparation of iron phthalocyanine, and this was followed quickly by a supplemental application de-

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scribing copper and nickel phthalocyanines, certain substitution products, and a recognition of the utility of these products for "coloration purposes—for example, padding, printing, or pigmenting."

The examination of the products of Dandridge, Drescher, and Thomas and the determination of their structure was referred to R. P. Linstead of the Imperial Institute of Science and Technology, London. The researches of Linstead and his students have resulted in a complete picture of the structure of this important new class of colored compounds, the development of synthetic methods, the determination of their properties, and the systematic extension of the whole new field of useful pigments and dyes which they represent. The first report of Linstead's work[5] to the chemistry section of the British Association for the Advancement of Science was made in September, 1933. Since that time his publications, plus a large number of patents assigned to various dye manufacturers, have described the series of compounds discussed below.

STRUCTURE

The fundamental nucleus of the natural coloring matters of the chlorophyll and hemin series is porphin (Figure 1). This compound is composed of four pyrrole nuclei joined in all the alpha positions by methine groups. Obviously it is structurally possible to replace any or all of these methine groups by nitrogen atoms, and the products thus obtained are known as azaporphins. The compound in which all four methine groups are replaced is known as porphyrazine, which can be named systematically as tetraazaporphin. Porphyrazine (Figure 1) contains eight equivalent hydrogen atoms (designated "H_e") attached to the pyrrole nuclei and two central hydrogen atoms designated "H_c." In the following listing of the compounds so far described, the porphyrazine structure will be used for purposes of reference.

Porphyrazines. Porphyrazine itself is not known, attempts at its synthesis having been unsuccessful[6]. Replacement of all H_e atoms by phenyl radicals yields octaphenylporphyrazine[6, 30]. In the latter compound, the two H_c atoms have been replaced by magnesium, tin, lead, and copper[6], yielding the metallo octaphenylporphyrazines. Likewise the copper and magnesium derivatives of octa-(*p*-nitrophenyl)-porphyrazine have been described[6].

Phthalocyanines. Obviously, in the porphyrazine structure each pair of H_e atoms theoretically can be replaced by a cyclic system, but in fact only compounds in which all four pairs have been replaced are described. The tetracondensed porphyrazines are represented in Figure 1, where R is a condensed ring system. The first and most important ring system of this type is that in which all four R's represent benzo groups. The parent compound of this group is tetrabenzotetraazaporphin, designated "phthalocyanine" (Figure 2) by Linstead. In this formula the sixteen equivalent hydrogen atoms attached to the benzene nuclei are designated as H_s (hydrogen capable of substitution) and the two central hydrogen atoms by H_c. This structural formula is based on chemical and physical studies[1, 35]. Phthalocyanine itself is now a commercial pigment, as discussed later.

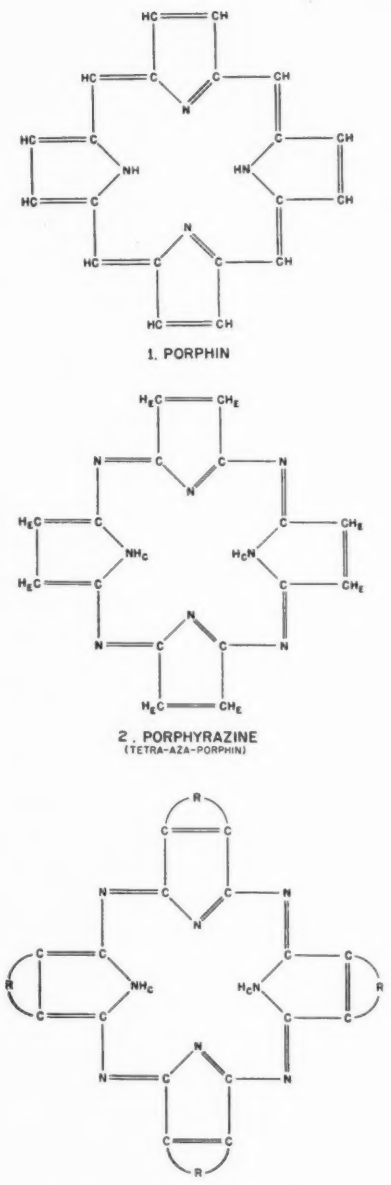

Figure 1. Structural Formulas

The H_s atoms in phthalocyanine have been replaced by halogens[28, 33, 36], sulfonic acid groups[18, 19], alkoxy groups[23], aryloxy groups[21, 22], amino and substituted amino groups[26, 29], phenyl groups[27], nitro groups[36], and azo groups[26].

The H_c atoms in phthalocyanine have been replaced by various metals[7, 17, 32, 37], including the mono- and dilithium and sodium phthalocyanines as well as the dipotas-

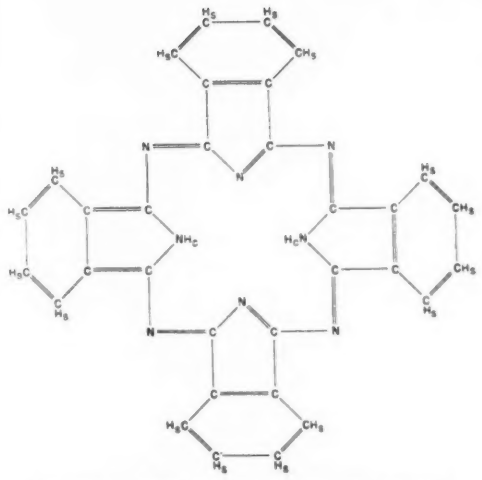

Figure 2. Phthalocyanine Structure (Metal-Free Phthalocyanine)

sium derivative. Among the divalent metals, the beryllium, magnesium, calcium, barium, zinc, cadmium, nickel, manganese, cobalt, chromium, lead, copper, mercury, stannous tin, and ferrous iron derivatives have been described. With metals of higher valence usually two of the valences of the metal substitute the H_c atoms, the remaining valences being satisfied by anions. Typical metal phthalocyanines of these classes are the aluminum, stannic tin, ferric iron, and vanadium derivatives. Copper phthalocyanine, a blue pigment, is now of considerable commercial importance, as will be discussed later in this paper.

Phthalocyanines in which the H_c atoms are replaced by methyl, ethyl and propyl groups have been prepared by treating phthalonitrile with the corresponding Grignard reagents[35].

Numerous metal phthalocyanines in which the H_s atoms are substituted have been described. Among the various halogenated phthalocyanines, tetra-(4)-chloro, octa-(3,4)-, (3,6)- and (4,5)- chlorometallo phthalocyanines have been prepared synthetically from the corresponding chlorophthalic acid derivatives[11, 38]. Copper monochlorophthalocyanine is obtained by action of cupric chloride on phthalonitrile, chlorination accompanying phthalocyanine formation[1, 9]; and analogous reactions occur with other metal chlorides. Direct halogenation has been carried out on copper, zinc, nickel, iron, and aluminum phthalocyanines, the degree of halogenation varying with the halogenation methods. Of these products, the copper phthalocyanine containing 14 to 16 chlorine atoms is of greatest interest. It is a green pigment, discussed in a subsequent section.

Various metal phthalocyanines have been sulfonated to yield alkali-soluble products[7, 18, 19]. In addition a copper tetrasulfophthalocyanine has been synthesized from the corresponding sulfophthalic acid[31]. The sulfonated products have been converted to alcohol-soluble dyes by conversion to amine salts[19, 31]. Sulfonated copper phthalocyanines also have been converted to insoluble metal salts and to lakes. The sulfonated copper phthalocyanines are discussed in more detail later in this paper. Metallophthalocyanines containing carboxyl groups also have been synthesized[38].

Tetra-(4)-ethoxy, tetra-(4)-methoxy, and tetra-(4)-phenoxy metallo phthalocyanines have been synthesized from the corresponding phthalonitriles[23]. Halogens in halogenated metallo phthalocyanines have been replaced by alkoxy and aryloxy groups[21].

Tetranitro metallo phthalocyanines have been prepared from 3- and 4-nitrophthalonitriles[11, 36]. Various acyl aminophthalocyanines have been prepared from the acyl aminophthalonitriles[26], and copper tetra-(4)-aminophthalocyanine has been prepared by hydrolysis of a copper tetra-(4-acyl-amino)-phthalocyanine[26]. Substituted aminophthalocyanines have been obtained from halogenated metal phthalocyanines by the action of primary and secondary amines[29].

4-Phenylphthalonitrile and substitution products have been converted to 4-phenyl metallo phthalocyanines[27]. Octa-(4, 5)-methylphthalocyanine has been prepared from 4, 5-dimethyl-1, 2-dibromobenzene[8]. 4-Benzoyl- and 4-naphthoylphthalonitriles have been converted to phthalocyanines, and the latter sulfonated to water-soluble products[20].

Numerous phthalocyanines have been described in which the 4-benzo nuclei are replaced by other ring systems. These included 1, 2- and 2, 3-naphthalocyanines[3, 4], tetrathiophenoporphyrazines[34], tetra-2, 3-thionaphthenoporphyrazines[34], tetrapyridinoporphyrazines[34], tetrapyrazinoporphyrazines[24, 34], and the phthalocyanine from 2, 3-dicyanodiphenylene oxide[23]. Attempts to prepare porphyrazines containing furan, pyridazine, pyrrole, isotriazole, or isooxazole nuclei have been unsuccessful[2].

Aza Porphins. Although they are outside of the scope of this paper, the synthesis of mono-, di-, and triazaporphins has been achieved recently[8, 12, 13, 15, 16]. These compounds contain one, two, and three nitrogens, respectively, which replace methine radicals in porphins.

METHODS OF PREPARATION

The fundamental reaction in all syntheses of phthalocyanine structures may be described as the interaction of a metal or derivative with an *o*-dicyano derivative of an aromatic compound or its equivalent. This reaction always leads first to the metal phthalocyanine, but demetallization may be an accompanying reaction or may be effected subsequently. The fundamental reaction may be expressed by the following equation:

4 aryl-$(CN)_2$ (or equivalent) + metal (or metal derivative) $\rightarrow$ metal phthalocyanine

This reaction may be carried out under a wide variety of conditions. For example, the undiluted *o*-dinitrile may be mixed with the reacting metal or metal derivative and the mixture heated to a suitable reaction temperature, at which point a vigorously exothermic reaction takes place with the formation of the phthalocyanine; or it can be carried out in inert solvents, in which case the reaction

rate and temperature conditions may be controlled more readily.

The fundamental reaction also may be extended to a wide variety of materials as equivalents of the *o*-dinitriles, conditions usually being such that intermediate formation of the nitriles may be postulated. For example, *o*-cyanobenzamides, *o*-halogenobenzonitriles, *o*-sulfobenzonitriles, *o*-dihalogenobenzenes, phthalimide plus ammonia or equivalents, and phthalic anhydride plus ammonia or equivalents all have been substituted successfully for phthalonitrile in the synthesis of phthalocyanines. Where active halogen or sulfonic acid compounds are used, a cyanide such as cuprous cyanide is supplied, and it is assumed that replacement of halogen or sulfo by cyanogen is the first step in the reaction.

A complete review of the synthetic methods is not desirable here, since the references cited under the various types of phthalocyanines describe adequately the possibilities in the synthesis of these compounds. The ease with which the unusual sixteen-membered ring is formed is startling. The synthesis of the phthalocyanines in the laboratory is much easier than that of the porphins, despite the widespread occurrence of the latter in nature and the apparent absence of the phthalocyanines. This is a striking instance of the development of a synthetic process parallelling a natural process but in the hands of the chemist being much more readily effected.

PROPERTIES

Phthalocyanine Pigments. The phthalocyanine pigments are all blues or greens; many of them are brilliant in shade whether judged as the crystalline colors or dispersed in various media. They are exceedingly insoluble in water and vary from totally insoluble to very slightly soluble in the usual organic solvents. The pigments are soluble in concentrated sulfuric and phosphoric acids, and in chlorosulfonic, anhydrous hydrofluoric, ethylsulfuric, and trichloroacetic acids; and in all instances they are reprecipitated by dilution with water. The products show amazing stability toward heat; many of them can be sublimed in a vacuum at temperatures of about 500° C.

The pigments also exhibit unusual resistance to chemical agents. Strong oxidizing agents result in scission of the ring systems, but the pigments show virtually no oxidative destruction in the atmosphere. Likewise, the pigments show a resistance to reducing agents, although a few members can be reduced under drastic conditions to a mixture of products which usually reoxidize readily to the original pigment. When tested in pigment applications, they all have good fastness to light, and certain members exhibit outstanding fastness.

Various substitution reactions have been attempted with the phthalocyanines, the greatest success being attained in halogenation and particularly in the chlorination of copper phthalocyanine to the green pigment discussed later. The pigments also can be sulfonated to products showing a fair degree of solubility in water and alkalies. The reactivity of the aromatic nuclei in the phthalocyanines is of a fairly low order; hence application of the Friedel-Crafts reaction to introduce alkyl and acyl groups has not been successful. Nitration of the pigments likewise is not successful, owing to the fact that the strong nitrating agents required act as oxidizing agents.

A recent publication of Helberger[14] discloses that certain metal phthalocyanines, as well as the corresponding porphins and azaporphins, exhibit brilliant chemiluminescence when oxidized under specific conditions. The phenomenon is most striking in the case of the magnesium derivatives. Interesting speculations can be made as to the possible relation of this emission of light during oxidation to the well-known role of light in the photosynthesis of natural products in the presence of magnesium-containing chlorophyll.

Soluble Phthalocyanines. The solubilized phthalocyanines, as typified by sulfonated copper phthalocyanine, show the expected solubility in water and alkalies. The colors are still brilliant blues to greens, the shades being shifted toward the green by sulfonation. The stability to light and other destructive influences of the soluble phthalocyanines is lower than that of the pigments, but the colors compare favorably with other acid colors of similar shade. On the other hand, conversion of the soluble phthalocyanines to insoluble metal salts and lakes improves their fastness properties, indicating that the unusual stability of the insoluble phthalocyanine pigments is in large part due to their very low solubility. The soluble phthalocyanines can be converted to salts of aromatic bases, yielding colors soluble in organic solvents. Sulfonated copper phthalocyanine and its derivatives are discussed later.

USES

The phthalocyanine pigments find application in virtually every field in which colored pigments now are used. These uses will be discussed in detail in connection with the pigments now commercially available. The soluble phthalocyanines have been converted to a wide variety of insoluble salts and lakes; these products also find wide application in the pigment field. In addition, the soluble types are being used in various ways in textile and paper dyeing; upon conversion to salts of organic bases, they are utilized as alcohol-soluble blues and greens.

PREPARATION OF COPPER PHTHALOCYANINE

By far the greatest commercial interest to date in colors of the phthalocyanine series involves the copper derivative, a new brilliant blue pigment of outstanding fastness properties. It was introduced first to the pigment trade at an exhibition in London in November, 1935, and American manufacture and trade introduction followed early in 1936.

As in every instance of a color pigment, manufacture consists of two distinct problems: (*a*) The synthesis of the compound itself and (*b*) the conversion of the colored compound to physical forms suitable for use in the

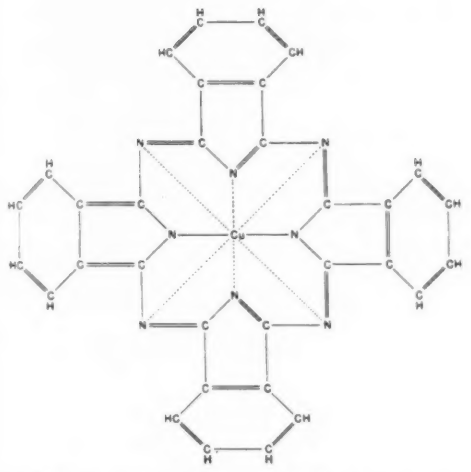

Figure 3. Copper Phthalocyanine Structure

many pigment outlets. This situation applies to an unusual degree to copper phthalocyanine, and new problems in synthesis and physical condition have been met and solved in the development of this product. The chemical structure of copper phthalocyanine is shown in Figure 3.

Synthesis. The general statements made in the section on the synthesis of phthalocyanines in general are applicable to copper phthalocyanine. The patent and periodical literature describe many methods of synthesizing the colored compound, but from a technical point of view three methods are important. The first is as follows:

Phthalonitrile + copper → copper phthalocyanine (1)

Phthalonitrile reacts readily under proper temperature conditions with finely divided copper to produce copper phthalocyanine. This is a two-phase reaction; hence intimate contact must be maintained during the reaction. Phthalonitrile melts far below the reaction temperature, and sublimes and polymerizes at a relatively rapid rate at the reaction temperature; hence problems of retaining the material in the reaction mass arise. Most serious of all is the exothermic nature of the reaction, which necessitates the design of high-temperature equipment in which proper temperature control can be achieved and the heat of the reaction can be dissipated readily. The reaction product is a hard solid of poor heat transfer properties, complicating still further the problem of maintaining proper contact of reactants and temperature control. When properly carried out, however, the method of manufacture results in excellent yields of a fairly pure color. The following method of preparation is quoted from the patent literature[11].

> Phthalonitrile and precipitated copper in the proportion of 4 molecules of the first to 1 atom of the latter are heated together at about 180-250° C. until pigment formation is complete. The reaction mass is freed from excess phthalonitrile by boiling with alcohol and purified from sulfuric acid.

The second method is based on the reaction:

Phthalonitrile + cuprous chloride → copper phthalocyanine + monochlorocopper phthalocyanine (2)

This reaction is similar in its operating characteristics to the preceding method except that the substitution of cuprous chloride for metallic copper results in a somewhat lower reaction temperature. This process can be operated with an excess of cuprous chloride, in which case the product is copper phthalocyanine + cupric chloride. Alternatively, it can be run with only slightly more than the theoretical quantity of cuprous chloride, in which case the reaction product is a mixture of copper phthalocyanine and monochloro copper phthalocyanine. The two pigments differ slightly in properties, the product containing the chlorinated material being slightly greener in shade. The following typical process is quoted from the patent literature[11]:

> A mixture of 12.8 parts of phthalonitrile and 2.5 parts of cuprous chloride is heated gently in a stream of nitrogen. A vigorous reaction takes place, and after a few minutes the mass becomes almost solid. This mass is allowed to cool, is broken, and is extracted with boiling water. After filtering, the residue is boiled successively with dilute acid and alcohol, filtered after each boiling, and finally washed with water and dried ....Besides the copper and cuprous chloride ...., cuprous and cupric oxide, cupric sulfide, cupric chloride, cupric acetate, and cupric sulfate may be used.

The reaction for the third method is:

Phthalic anhydride + urea + cupric chloride catalysts → copper phthalocyanine (3)

This ingenious method of preparation, the chemistry of which is not understood thoroughly, was developed by Wyler of Imperial Chemical Industries. The operation consists in melting together phthalic anhydride, urea, cupric chloride, and catalysts such as boric acid. The mass is heated under fusion conditions; water, ammonia, and carbon dioxide are evolved, and a good yield of copper phthalocyanine of good quality is obtained by working up the reaction mass. The following typical preparation is quoted from the patent literature[39]:

> One hundred and thirty parts of urea, 5 parts of boric acid, are melted together with stirring. When the temperature reaches 150° C., a mixture of 100 parts of phthalic anhydride and 20 parts of cupric chloride (anhydrous) is added. The mass is then heated to 200° C. till formation of coloring matter is complete. It is then cooled, ground, and washed with hot dilute aqueous caustic soda, then with hot dilute aqueous hydrochloric acid. The pigment so obtained is not finely divided enough for use, and is accordingly dissolved in about eight times its weight of sulfuric acid (specific gravity 1.84). The solution is poured into water (about enough to give eventually 5 per cent sulfuric acid). The diluted suspension is filtered, and the paste washed with water. This paste is preserved for use or dried according as an aqueous pigment paste or a dry powder suitable for mixing with nonaqueous substances is desired. The yield of copper phthalocyanine is 65 parts.

In all of the three methods outlined above, copper phthalocyanine is obtained as a bright blue exceedingly insoluble compound which is of little or no value as a color pigment. The product may be purified—for example, by a vacuum sublimation—and obtained as brilliant blue needles, still of little value as a pigment. When ground into printing inks, paints, etc., or used for the coloring of rubber, paper, etc., the compound in this form is dull in shade and exceedingly weak tinctorially. For this reason the compound must be subjected to physical treatment to produce different types adapted to application in the various fields.

Physical Conditioning. As disclosed by de Diesbach and amplified by Linstead, copper phthalocyanine dissolves readily in concentrated sulfuric acid and is reprecipitated on dilution with water. This behavior is entirely comparable physically with the "acid pasting" of vat colors, widely practiced in the dye industry. However, changes in chemical structure apparently occur in the process along with the physical changes usually expected, and the conversion of copper phthalocyanine to useful pigment types depends entirely on proper application of the acid-pasting procedure.

The usual practice consists in treating the pigment with concentrated sulfuric acid, in which it dissolves as the green sulfate. This solution is run into a large volume of water, resulting in the precipitation of the sulfate, followed by hydrolysis of the latter to free copper phthalocyanine. When precipitated in this way, the crystal structure of the pigment is altered, and the dimensions of the primary particles are reduced to a very low order. Conditions for this acid pasting may be varied over a wide range; more recently it has been found that other agents such as chlorosulfonic acid, phosphoric acid, and anhydrous hydrogen fluoride may be substituted for sulfuric acid. When the proper selection of conditions and solvent is made, the pigment is obtained as a water-wet paste in a highly dispersed form.

The water-wet paste is supplied at the present time to the pigment trade for use in the preparation of lakes by adsorption on aluminum hydroxide, barium sulfate, rosinates, and similar extending agents. The paste form also is subjected to further dispersion, mixed with water-soluble diluents, and dried; a dry product results which disperses in water to colloidal solutions. This product is used particularly for paper coloring and the preparation of water paints. The wet pigment also is dispersed in rubber latex and the latex is coagulated, yielding a dispersion of the pigment in rubber which is used for rubber coloration.

If the paste form is dried in a normal manner, an exceedingly hard solid is obtained; and even though this solid is ground very fine, the dry color is difficult to incorporate into printing inks, paints, and similar nonaqueous media. Extended grinding in the vehicle is necessary to obtain the full color value of the dried pigment. For this reason, methods have been devised for retaining the dispersion of the wet pigment during the drying process; a dry powder is obtained which wets out and disperses rapidly in nonaqueous media, and which develops its full color strength with a minimum of grinding.

PROPERTIES OF COPPER PHTHALOCYANINE

Copper phthalocyanine in the crystalline form is deep blue in color with a strong bronze reflection. The dry dispersed types of the pigment are brilliant blue powders, the surface bronziness disappearing almost completely. The pigment is insoluble in all ordinary solvents with the exception of concentrated sulfuric, phosphoric, chlorosulfonic, ethylsulfuric, and trichloroacetic acids. This insolubility persists even at high temperatures in organic solvents such as hydrocarbons, esters, alcohols, and ketones. The pigment has extreme stability to heat, is highly resistant to acids and alkalies, and is little affected by oxidizing and reducing agents except under drastic conditions.

Of perhaps greatest interest to pigment users is the fact that copper phthalocyanine is exceedingly close to the ideal pure blue, since it absorbs almost completely the red and yellow portions of the spectrum, reflecting only blue and green bands.

The high tinctorial strength of the pigment, as judged in various media, deserves comment. When judged in light and medium shades, the color is approximately twice as strong as the iron blues and twenty to forty times as strong tinctorially as ultramarine. When deep shades are evaluated, the inherent strength of a color is not the major factor, and these values do not hold. In deep shades copper phthalocyanine suffers from the fact that it is still too strong to give the desired "bulk" in finishes; it also exhibits the troublesome bronziness characteristic of the older iron blues.

USES OF COPPER PHTHALOCYANINE

The properties of copper phthalocyanine made it inevitable that, if available at proper cost, it would find rapid adoption in the usual color pigment applications, among which the following are particularly important:

Printing Inks. The pigment already is used widely in the printing ink field, having replaced in part the iron blues and various basic color lakes. Inks containing this new pigment equal the most brilliant products previously available, and the fastness of the colors thus produced far surpasses that of the products replaced by this new pigment. The pigment also has solved a difficult problem—the provision of a suitable blue for three-color printing. At first, considerable difficulty was encountered with the physical properties of the printing inks, but this has been overcome by special processing of the pigment as well as by suitable reformulation of the inks.

Artists' Colors. Copper phthalocyanine immediately was adopted for artists' colors since, in addition to its remarkable fastness properties and brilliance, it is the first blue to show proper shading effects under both natural and artificial light.

Paints, Lacquers, and Enamels. Copper phthalocyanine is being adopted rapidly in the formulation of colored finishes. Great difficulties have been experienced in the past with the poor fastness to alkalies of the established iron blues and the poor fastness to acids of the important ultramarines, especially when used in light shades; and the light fastness of both of the old types left much to be desired. Likewise serious difficulties have been encountered with changes in the shade and other properties of the old color pigments upon storage of the coating compositions containing them (poor "can stability"). Copper phthalocyanine has overcome many of these difficulties. For use in finishes, as well as in artists' colors and printing inks, dry

powder types of the new pigment have been provided which develop their full strength with very little grinding in the oil media.

Water Paints are finding increased use, particularly in the coloring of plastered surfaces. Copper phthalocyanine makes available a brilliant blue in this field which is unaffected by the alkaline conditions destructive to most available color pigments. A similar use is incorporation of copper phthalocyanine in cement building materials and composition floorings.

Coated Textiles. Brilliant blue coated-textile fabrics, used especially for book covers and tablecloths, are being produced using copper phthalocyanine as the color pigment. Its fastness to acids and alkalies means that soaps, acid fruit juices, and similar agents do not affect the colored fabrics, and of course fading on exposure to light is at a minimum.

Paper. The new pigment has found wide use in the production of brilliant blue coated papers and in beater dyeing of paper pulp; in each case the combination of brilliance of shade and fastness to all destructive agencies surpasses anything previously available. Of special interest is the rapid adoption of the pigment in the preparation of wallpapers, where exceptional light fastness and brilliance, even in light shades, is demanded. Actually, copper phthalocyanine provides the first blue pigment meeting the desired fastness standards. For use in paper coloring, the pigment has been provided in the form of a powder which disperses almost instantly in water to a colloidal solution.

Linoleum. The severe conditions to which linoleum is exposed during manufacture and use make a heavy demand on the color pigments used in its production; yet copper phthalocyanine makes available permanent deep shades of reddish blue and light shades of greenish blue.

Rubber. Copper phthalocyanine was adopted immediately in the rubber trade for the production of brilliant shades of blue, ranging from deep reddish blues to greenish pastel shades. The color is fast to all conditions of vulcanization, offers no difficulty due to migration, and, broadly speaking, meets all the requirements of rubber processing. It is of particular interest that, although the pigment contains copper and that even traces of ionizable copper catalyze the destruction of rubber, copper phthalocyanine is without effect. This is a striking proof of the "tight" nitrogen-to-copper bond in the molecule.

Plastics. Its stability toward heat plus its unusual resistance to the other chemical and physical conditions encountered in the preparation of plastics make copper phthalocyanine particularly valuable in this field. Its utility has been demonstrated in phenol-formaldehyde, methacrylate, casein, acetate, and numerous other types of plastics.

Textiles. Where pigment colors are used for textile printing, and where it is necessary to impart a temporary color to certain yarns in the manufacture of woolens and worsteds, copper phthalocyanine has been found suitable. Abroad the pigment is incorporated in viscose and acetate spinning baths, and results in the production of synthetic yarns permanently colored by the pigment dispersed in the filaments.

The iron blues and ultramarine have been in use in tremendous quantities for a century or more, filling nearly all the requirements for blue pigments. For certain specialties where brilliant shades have been desired the fugitive lakes of basic colors have been utilized. And in the few cases where their cost is not prohibitive and their dullness is not too objectionable, vat dyes have been used where special demands have been made for fastness. However, none of the above products combines the brilliance, fastness to all destructive agencies, and moderate cost of copper phthalocyanine, and it appears inevitable that this already important pigment will displace its predecessors to a much greater extent.

PREPARATION OF CHLORINATED COPPER PHTHALOCYANINE

As soon as copper phthalocyanine became available, the next interest in the phthalocyanines was directed toward possible chemical modification of this color. It was logical that attempts would be made to introduce halogen into the molecule, and such studies quickly led to the discovery that the highly chlorinated pigment is a brilliant green possessing the same outstanding fastness properties as the parent blue pigment.

As in the case of copper phthalocyanine, it was necessary to devise methods of producing the chlorinated pigment and processes of converting the pigment to the various physical forms which would make it suitable for pigment use.

In developing the green pigment the first necessary decision was the determination of the degree of chlorination required. These studies resulted in the observation that the chlorination of copper phthalocyanine results in gradual greening of the blue shade but that a green rather than a greenish blue is not obtained until at least twelve chlorine atoms are introduced into the benzene nuclei of the parent pigment. Further work indicates that the best pigment contains fourteen to sixteen chlorine atoms per phthalocyanine unit, sixteen being the saturation point. The next question involved was a decision as to whether the chlorinated pigment should be produced by chlorination of copper phthalocyanine or by chlorination of the intermediates for phthalocyanines, followed by application of the usual phthalocyanine syntheses to the chlorinated intermediates. Little success was achieved in the conversion of polychlorinated phthalic acid derivatives to chlorinated copper phthalocyanines; hence, as is shown by the patent literature, the preparation of the pigment has been achieved by chlorinating copper phthalocyanine.

The introduction of chlorine into copper phthalocyanine involves several new problems; the most important are associated with the extreme insolubility of the starting material in the customary chlorination solvents and the low degree of reactivity of the hydrogen atoms in copper phthalocyanine. At ordinary temperatures the only ob-

served effect of chlorine on copper phthalocyanine is one of oxidation; this is encountered to a serious degree when the pigment is dissolved in sulfuric acid and treated with chlorine in the presence of carriers such as iron salts. Direct chlorination to the necessary degree, therefore, must be carried out at relatively high temperatures and under anhydrous conditions in order to prevent oxidation. Among the many methods of chlorination described in the patent literature, the most feasible are the chlorination of copper phthalocyanine suspended in phthalic anhydride, chlorination of the pigment suspended or dissolved in molten sodium aluminum chloride, and the direct action of liquid chlorine on the pigment under pressure. All of these processes are practical and can be operated on a manufacturing scale, but it is probable that continuing research will disclose other and perhaps more readily operable manufacturing procedures.

Physical Conditioning. All that was stated in the preceding section about the physical conditioning of copper phthalocyanine is equally applicable to the chlorinated pigment. The product obtained from the chlorination process is of little value as a color pigment; its strength is low, shade is very dull, and texture is unsatisfactory. However, application of approximately the same acid-pasting conditions to the chlorinated pigment as are used with copper phthalocyanine results in the dispersion and other physical and chemical changes that yield the valuable green pigment. After the physical state of the pigment has been altered by acid pasting, it again has been found necessary to convert the so-treated pigment to various paste and powder forms particularly suited to the pigment outlets.

PROPERTIES OF CHLORINATED COPPER PHTHALOCYANINE

Chlorinated copper phthalocyanine containing approximately fourteen chlorine atoms per phthalocyanine unit, in the crystalline form, is a deep bluish green, almost black, with a strong bronze reflection. The dry dispersed types of the pigment vary from deep bluish greens to bright bluish greens, depending upon the type of dispersion and dilution. The pigment is almost totally insoluble in organic solvents, even at very high temperatures, and is soluble in concentrated sulfuric, phosphoric, and chlorosulfonic acids. The solubility in these acids is somewhat less than that of copper phthalocyanine itself. The pigment also has extreme heat stability, although purification by vacuum sublimation has not been disclosed. The color is highly resistant to acids, alkalies, and oxidizing and reducing agents except under drastic conditions not encountered in pigment use. The halogen atoms are tightly bound but can be replaced by other substituents or by hydrogen under some experimental conditions.

To the user, the importance of the pigment other than its extreme fastness is the fact that it is a brilliant bluish green of high tinctorial value. Its purity of shade is comparable with that of copper phthalocyanine.

USES OF CHLORINATED COPPER PHTHALOCYANINE

Although this pigment has been available to the pigment trade for only a few months, its importance will be apparently of the same order as that of copper phthalocyanine. It is unnecessary to repeat the details of the various uses, since they are entirely comparable with those of the blue pigment. It will suffice to say that in printing inks, artists' colors, paints, lacquers, enamels, and other finishes, water paints, coated textiles, paper, linoleum, rubber, and specific textile uses this pigment makes possible the production of brilliant green shades with fastness properties hitherto unavailable. In such uses the pigment will replace the well-known chrome greens, chromium tetrahydroxide greens, Pigment Green B, and the various lakes of basic colors. The tinctorial strength of this pigment is as much as twenty times that of the pigments it is displacing. The shade is described as a bluish green. For yellower shades of green, the pigment is being mixed with the numerous greenish yellows of excellent fastness already well known to users.

This pigment is being provided in the several physical types corresponding with those of copper phthalocyanine referred to in the preceding section. The pure pigment is available in a soft powder form that develops its full strength rapidly in the various nonaqueous media. It is available as an aqueous paste for conversion to extended types and also has been converted to a water-dispersible dry powder which yields a colloidal solution almost instantly; this type is particularly suitable for paper coloring.

Green always has been considered an attractive color, and the dye and pigment industries have carried out continuous research on the development of brighter and faster green pigments. However, all products available up to the present have been unsatisfactory when brilliant shades and excellent fastness properties have been desired. It is therefore obvious that chlorinated copper phthalocyanine will become established very quickly as an important member of the color pigment series.

PREPARATION OF METAL-FREE PHTHALOCYANINE

Usually the simplest member of any series of dyes or pigments receives the first commercial attention. However, in the case of the phthalocyanines, phthalocyanine itself, more generally known as metal-free phthalocyanine, received attention only after the copper derivative had been developed. This was due in part to synthetic difficulties but more because of the circumstances, already related, attending the discovery of the copper compound.

As in the instances discussed above, it was necessary to devise methods of preparing the metal-free pigment and also methods of converting the compound to the proper physical types.

The patent literature contains several disclosures of the preparation of metal-free phthalocyanine. These are of two

(Continued on page 620)

PROCEEDINGS OF THE

American Association of Textile Chemists and Colorists

OCTOBER 16, 1939

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• CALENDAR • OF COMING EVENTS

Fall Meeting, Mid-West Section, afternoon session—3:00 P. M.; evening session—7:00 P. M., Hotel Sherman, Chicago, Ill., October 21, 1939.

* * *

Meeting, Philadelphia Section, Penn Athletic Club, October 27, 1939.

* * *

Meeting, New York Section, Swiss Chalet, Rochelle Park, N. J., October 27, 1939.

Fall Meeting, South Central Section, Andrew Johnson Hotel, Knoxville, Tenn., December 9, 1939.
(This is the date of the Auburn-Tennessee football game.)

* * *

Annual Meeting and Convention, auspices New York Section, 1940. Date to be announced later.

Tintinol Process*

H. L. SIEVER**

THE constantly increasing use of various types of cut silk, viscose rayon, cellulose acetate, rayon and their admixtures with cotton, wool and silk has made necessary some simple method of tinting the fiber for identification in the mills, because of the many combinations in process of manufacture at the same time.

Cut staple fiber is a continuous filament of rayon made into lengths suitable to cotton mill machinery. It is opened into a fluffy mass and baled for the market in the same manner as a bale of cotton.

The demand for this type fiber in textiles has opened a field to all cotton mills, many of which are without dyeing facilities. To install conventional dyeing equipment for this purpose alone would require a substantial expenditure. On the other hand, mills who have the customary cotton raw stock dyeing equipment find that its use for tinting is too expensive and in addition is injurious to the fiber. The extra handling is costly and the heat necessary in drying produces a harsh, wiry, dry condition that deadens its natural character, so that when blended with undyed white fiber, the spinning qualities are greatly impaired.

The manufacturers of cut staple viscose rayon and acetate rayon endeavor to finish the fiber, in a manner of their own, for good running qualities in the mill, but if this stock is subjected to dye liquor and heated to high drying temperatures, the finish is apparently destroyed in the dye bath, therefore when blended with the natural fiber, to obtain a tint, the good running qualities of the natural fiber is diminished to the extent of the blend, while with the Tintinol Process the original condition is not disturbed.

Artificial fibers, unlike cotton, are without a natural lubricant and for this reason are more susceptible to moisture. Unless they are treated to retain a desirable amount of moisture and lubricant they are difficult to card and spin.

In this respect the Tinting Process offers three desirable factors, namely: moisture, in many cases fiber lubrication, and color tinting. With these factors available and when applied in the opener rooms the treated stock is sufficiently mixed at the pickers, so that the mass of fibers take on a characteristic tenacity similar to good running cotton.

The tinting fluids used with the process are known as Tintinols. The dyestuffs used are the result of considerable research in the fugitive dye field. They are selected with the idea of maintaining the maximum fugitive value for viscose rayon, acetate rayon, cotton, wool and silk and mixtures of these fibers.

The object is to produce the brightest possible color with a given amount of fluid (about 2 per cent on the weight of stock) so that various shades, with less intensity, can be had by applying less fluid and at less cost to the mill.

However, a fugitive tint sufficient for identification is not the only requirement. There are other commercial values to be considered. Dye preparations when made up with fiber conditioning fluids, should not bleed excessively at the slasher. They should not contaminate the sizing mixture but they should react favorably to pollution requirements and in disposal plants. The Tintinols are manufactured at one source where it is aimed to meet these requirements and to maintain a constant composition, thus assuring the trade an unusual uniform certified fugitive dye.

The process eliminates the necessity of any separate dyeing operation, heating, extracting, drying or mixing of the stock. The stock is simply run as usual and tinted at the same time.

Mechanical equipment for this process should be designed to operate constantly and over a period of time without danger of corrosion, leaks or stoppage. The equipment consists of a mechanical unit which is attached to and synchronized with one or more fiber blending machines.

The "Tintinols" fugitive to all natural and synthetic fibers, are shipped out in the same style containers ready for use. These are arranged in series, usually: Red, Blue, Green, Yellow, Orange, Purple, Grey, etc., and connected to one and the same pipe leading to a special metering pump, which forces the tinting fluid under pressure to the sprayheads.

By manipulating a graduated mechanical measuring valve the quantity of tinting fluid is determined accurately to each hundred pounds of stock passing into the mill.

To change from one color to another, when a new batch is ready to run, it is only necessary to turn a valve. Compressed air is used both to atomize and return the fluid to the proper reservoir.

*Presented at Annual Meeting, Boston, Mass., September 15, 1939.

**Borne Scrymser Co.

The process is simple in operation, economical and efficient. The mechanical equipment is furnished to the mills without charge.

DISCUSSION

President Eavenson: Are there any questions you would like to ask Mr. Siever?

That is a very interesting process. It seems very simple, and it ought to be readily understandable.

Mr. Caldwell: Are the tints soluble like mineral and vegetable oils?

Mr. Siever: We have two classes of them: those that are soluble with oils and those that are soluble with water.

Mr. Caldwell: Do you sell them as the dry tints, or with oil dispersion?

Mr. Siever: Both—with oil dispersion and certain other things that we incorporate with the water.

Mr. Caldwell: Is it possible to get the tint and mix it with your own oil?

Mr. Siever: No, it isn't.

Mr. Caldwell: They are already dispersed and ready for use?

Mr. Siever: Yes, they are.

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The Dyeing of Staple and Spun Viscose Rayon*

CHARLES B. ORDWAY**

INTRODUCTION of new fibers and fabrics to the textile industry requires a long period of experimentation before the dyers find at least temporary methods whereby the processing may be carried out so that it will meet the consumer's requirements.

The textile chemist and dyer were given in staple and spun viscose rayon, a cellulosic fiber similar in chemical nature as cotton, but distinct in physical characteristics from cotton. Taking their cue from the chemical nature of viscose rayon they used procedures that were run on cotton goods. But met with varying amount of success until they began to take into full consideration the physical nature and characteristics of these viscose rayon fibers as compared to cotton fibers.

The physical characteristics of viscose rayon that are mainly responsible for these differences in dyeing procedures between cotton and rayon are:

1—Viscose rayon fibers swell upon wetting out, heating, and in an alkaline bath this swelling is more pronounced than a neutral one.

2—Viscose rayon is a filament fiber of cylindrical nature, while cotton is a hairy fiber of flat and curly nature.

3—Viscose rayon is practically a pure cellulose, and exerts great capillary attraction for colors, while cotton has natural waxes and pectins that retard the affinity of the dyestuff for the cellulosic fiber unless the cotton is properly scoured or wet-out.

4—Wet-out cottons at low or high dyeing temperatures lose no strength, while viscose rayon fiber's strength is reduced materially in the wet-out condition.

Dyers found out that changes from the established cotton dyeing procedures were necessary and some of the first changes made that gave fairly satisfactory results were:

Substantive (Direct) Colors: By carefully selecting those colors that exhaust slowly and give full color value at lower dyeing temperatures. Lower dyeing temperatures and shorter dyeing periods were found preferable to rapid exhausting and high temperature dye bath as preferred for cotton.

Diazo and Developed Colors: The same points hold true on these colors as on directs.

Sulfur Colors:

1—Selection of colors that exhaust slowly and fully at lower temperatures than used on cotton methods.

2—Use of retarding agents for obtaining level dyeing.

3—Reduction in alkalies, salt, and other chemicals on dyeing formula as compared to cotton.

4—A reduced amount of staple rayon can only be dyed in raw stock machines as compared to a larger amount of cotton and this is due to the swelling of the rayon fibers during the dyeing operations.

Vats: Similar changes were necessary for vats as sulfurs, but on the cold dyeing vat colors it was found advantageous to increase the dyeing temperatures as compared to cotton.

Naphthols:

1—The naphthol bath was found to work advantageously at higher temperatures than used on cotton methods so as to obtain satisfactory penetration on rayon.

2—The alkaline content of the naphtholate bath was kept to a minimum due to the swelling effect of caustic on the viscose rayon fibers.

3—Selection of bases and salts for levelness in development at 90° F.

*Presented at Annual Meeting, Boston, Mass., Sept. 16, 1939.
**Technical Dept., American Aniline Products, Inc.

During the past few years, the dyestuff makers have realized that viscose rayon in the staple and spun form is a distinct fiber with special dyeing characteristics.

The dyestuff makers have brought out color cards of the older types of colors that represented selected dyestuffs best suited for the dyeing of staple and spun viscose rayon in the different forms.

These selected groups have proven quite valuable as they give good color value and level dyeings on these distinct rayon fibers, but have certain weaknesses as to fastness requirements, subsequent manufacturing operations, time period for dyeing operation, effect on dyeing equipment, and dyestuff costs.

The *Substantive (Direct) Colors* are the simplest to apply, but do not possess sufficient washing fastness to meet the fastness test that the finished rayon fabrics require. There are some of the more expensive fast-to-light direct colors that are fairly satisfactory to washing, but they are too expensive for dyeing most fabrics unless a high light fastness is required.

Diazo and Developed Colors give good to excellent wash fastness and moderate light fastness but they are quite expensive both as to dye and chemical costs, the dyeing process requires a greater time and labor cost, and the diazo bath shortens the life of the dyeing equipment materially.

Sulfur Colors offer very good to excellent wash fastness with only fair light fastness but they do not leave the rayon fibers in the best condition for subsequent manufacturing operations. The dyeing time required for sulfurs approximates that of the developed colors. The range of shades is quite limited on the sulfur colors.

Vat Colors are eliminated largely due to price and time required to process.

Naphthol Colors are quite expensive but are used to fill in the groups not covered by the sulfur colors, but as a group they are too expensive for regular use.

A textile manufacturer, when he decides on the manufacture of spun rayon fabrics is naturally desirous of using only those dyestuffs that require the least number of dyes and chemicals for obtaining the desired range of shades.

He also wishes to use those dyestuffs and dyeing methods that are the most economical as to:

1—Dye and chemical costs.

2—The time and labor costs.

3—Giving the most desirable operating conditions for subsequent manufacturing operations after being dyed.

4—Obtaining the desired fastness to washing and other requirements.

5—The upkeep costs on the dyeing equipment (this refers to the dyeing process' chemical reaction, if any, and how they affect the life of the materials of which the dyeing equipment is constructed).

The American Aniline Products, Inc., as dyestuff makers, have seen the need of bringing out a new and complete range of dyestuffs designed particularly for staple and spun rayons. With this as their objective, this manufacturing organization is now offering to the dyeing industry a range of dyestuffs known as the *Formanils*.

These Formanil colors are dyed directly as regular substantive colors and then aftertreated with formaldehyde at 120-140° F. for twenty minutes, rinsed hot, and finished.

We feel in offering these colors that they meet the demands for simplicity in application, economy in dyestuff, chemical, labor, and time costs.

The dyeing process has no deteriorating or corroding action on the metals or materials of which the dyeing equipment may be constructed, such as the valves, pump, etc.

On the older types of direct dyed and aftertreated colors, the aftertreated shades changed considerably from the unaftertreated and were usually much duller.

The Formanil colors show no particular change on aftertreatment and are not dulled to any extent except when acetic or formic acid is used in the aftertreatment bath with an excessively high aftertreating temperature. The addition of acetic acid to the aftertreatment bath is not recommended as it shows no particular value at the present time.

Formanil colors offer exceptional opportunities of application to novelty spun viscose rayon goods, containing wool rabbit hair, silk, or Celanese, as they may be dyed in union shades or effect color combinations by this simple dyeing method without injury to the effect fibers used in combination with the viscose rayon.

It would be quite difficult and would require special control methods to process similar types of novelty spun rayon fabrics using developed, sulfur, or vat colors as the Celanese, silk, rabbit hair, or wool would probably be affected by one of these dyeing processes.

The dyeing of spun rayon yarns in its many forms such as skeins, warps, packages can be handled by selecting those colors particularly adapted to each method of dyeing.

The same thing applies on dyeing raw stock or staple rayon, the colors are selected for this particular type of processing.

Piece goods dyed on the jig or box also require colors that leave Celanese, wool, and silk resisted; on novelty fabrics many shades can be obtained with the Formanils that meet this special requirement.

On plain spun viscose rayon piece goods, it is very necessary to have colors that will give good white discharges on printing. The Formanils offer a good range of shades for this purpose and are quite economical on some of the heavier shades in comparison to developed shades.

For novelty half hose containing spun viscose rayon, mercerized cotton, Celanese, silk, or wool, Formanil colors have proven quite valuable in giving improved wash fast

ness plus the resist or multi-colored effect as requirement demands.

These are a few of the fields in which these new colors have proven of value to dyers on processing spun viscose rayon in its different forms.

Mill officials will find that these colors should prove very helpful in meeting new specifications for washing, perspiration, light and other fastness tests, that spun rayon materials may be required to meet in the future.

NOTE: Since preparing this paper, our development department has brought out a series of new Formanil Browns and a range of Formanil Violets giving a red to bluish range of violets. These new violets should prove invaluable to processors of spun and staple rayon materials as they possess the Formanil rating as to the various fastness properties.

Physical Testing

in the Textile Industry*

DR. ERWIN J. SAXL**

PHYSICS as it applies to the textile industries, has made substantial progress in recent years. Despite the fact that the records of the primitive art of weaving go far back to old Egyptian history, and that dyeing is so old an art that its creation has been adorned in artistic myth (the fable of the discovery of purple)—it is only in the last decades that an attempt was made to learn more about the basic laws that are at the fundament of all textile engineering.

The thanks of the textile industries are to be given in this connection to the chemists who taught us about different dyestuffs, scientific procedure, and synthetic textile materials. While the general approach to scientific problems in this field was originally a chemical one, it is becoming gradually clear that fabrics are largely physical products, provided always that it is possible at all to differentiate between modern chemistry and physics . . . which in reality are just two facettes of the same crystal.

SOME PHYSICAL CHARACTERISTICS

When we buy a piece of textile material, be it in the form of a dress, stockings, a sweater, aside from styling, this material can be described perhaps most easily in terms of its physical characteristics. The chemist may have spun the synthetic fiber and dyed it, but the customer goes into the store and buys the cloth not because it is "cellulose xanthate" or has been treated with sulfurylchloride but because it *looks, feels* and *drapes* nicely, *reflects* the color properly, and is *warm*, despite the fact that its *porosity* provides for proper ventilation.

When we buy a textile material we want *high tensile strength, high resistance to wear and abrasion*, a given *softness, resistance to crushing*, and a *color that resists bleaching* under the influence of the electro-magnetic waves as they pertain to the visible part of the total spectrum. The success of some well known textile materials in the past few years was due frequently to physical reasons. Reference may be made for instance to tropical worsteds—that is to say (physically speaking) to materials that have the excellent crush resistance of worsteds combined with small heat retentivity due to their high porosity.

These are the actual, physical terms that are significant for the practical conditions under which a material is to be worn. Therefore, it has great practical significance to realize what is the actual criterion that makes a piece of material desirable to the customer, and then to specify on a construction that can be reproduced at any time at will, in the mill, exactly as wanted by the final purchaser.

In view of this status of the matter, the chemist, the textile man, and the consumer are today becoming more conscious of the physical characteristics that increase the value of textile materials. It is therefore appropriate to submit here some new and improved methods of definite physical approach whereby it is possible to evaluate these characteristics, to improve them, and later to check them. In this manner the testing instrument becomes of definite significance in an attempt to improve our products, for standardizing, and for aiding in the actual merchandising.

If we consider textiles as physical materials, we may be permitted to describe them in physical terms.

PHYSICAL TESTING APPARATUS

One of the most important of their characteristics is their flexibility. When buying a piece of cloth, for instance in the form of a suit or dress, one of the most important tests is the "touch-test," that is, taking the material into the hand and crushing it. What actually happens in the material under these conditions?

We have to deal here with the resistance to deformation under the influence of weight and of flexural forces. Stiffness Testers such as the one shown here make possible the evaluation of the factors of stiffness, softness, crush resistance, permanent deformation, elasticity, draping and elastic recovery. The same instrument can be used for determining the above factors for yarns as well as fabrics. For

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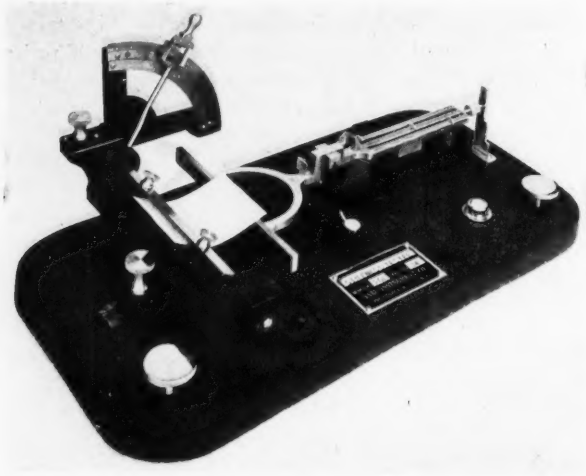
**Consulting Physicist and Chemist.

the mathematical discussion of the phenomena the reader is referred to the literature. (1).



Stiffness Tester

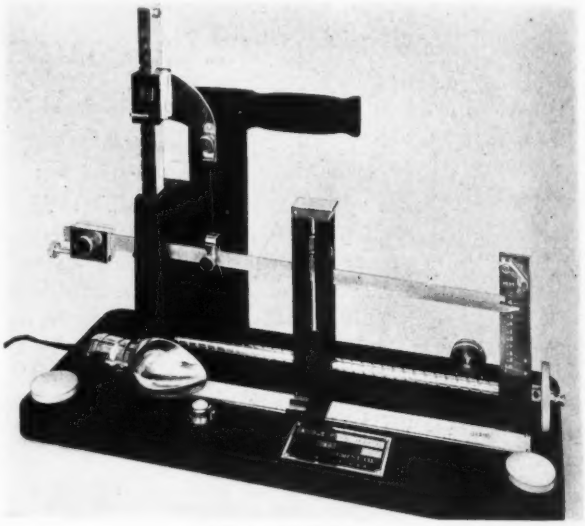
The instrument shown serves for establishing load vs. deflection characteristics. This machine is adjustable for most types of materials by changing the gap length, the deflecting angle, and the force of deflection (weight).

Fabrics resist not only elongation but compression. This is particularly important if we are dealing with the original staple, and pile fabrics. The recovery from vertical compression is one of the most significant factors for textile materials. In order to determine this in a fabric, another instrument was designed.

This same manner of measuring load vs. compression may be used for rolls of cloth, folds of cloth, rugs, turkish towels, velvets, rayon staple, gelatine, etc. Again, for a detailed analysis of the physical principles involved, the reader is referred to the literature. (2).

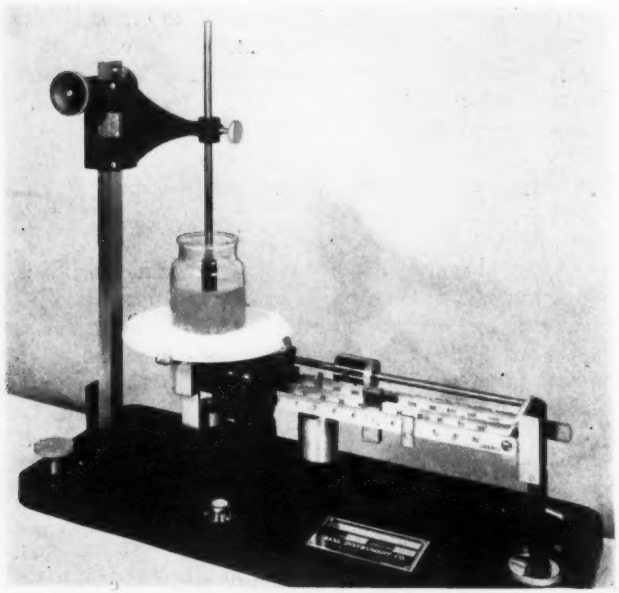
Other developments made recently are:—

A small precision instrument for testing the breaking strength and yield point, not only of *bundles* of staple or cotton, but of *single fibers*. Inasmuch as a chain is never stronger than its weakest link, the knowledge of the individual fiber of which the finished yarn is composed, before the yarn is spun, is a time and money saver for the manufacturer. Refer to literature. (3).



Single Fiber Tester

Another instrument for improving yarn quality is the Tension Meter.

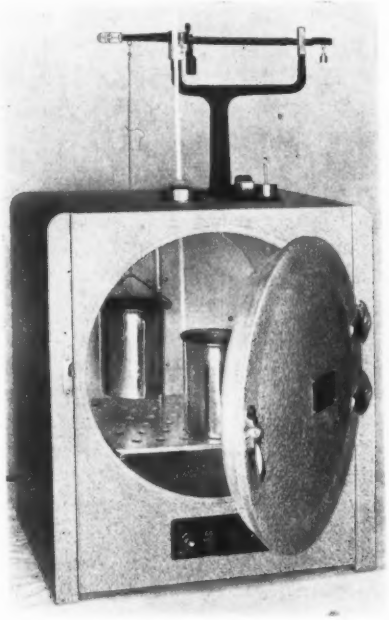


Compressometer

Tension Meter

Control of tension in spinning is made possible by the use of this. Thus lighter shades due to overstretching during spinning, warping and slashing (for which the dyer frequently is blamed unjustly) can be avoided by systematic and simple tension control. Equally, filling bars can be eliminated by controlling shuttle tension with the tension meter.

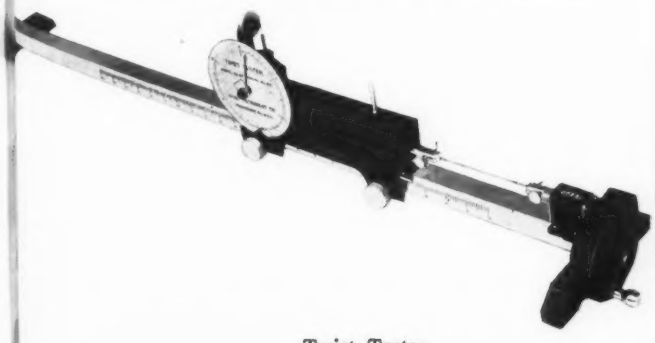
It need not always be an entirely new instrument that becomes of engineering significance. Frequently improvements on well known methods make them more practical and facilitate their general application and usefulness.



Conditioning Oven

Among these may be mentioned a Conditioning Oven with new features. By using a circular streamlined heating element a very even drying and improved circulation results, thus avoiding overconditioning and simultaneous underdrying in different parts of the sample. A more sensitive balance makes it possible to use smaller samples, resulting in quicker tests, thus speeding up and making more precise the determination of water in cloth samples, rayon flock, cotton and other textile materials.

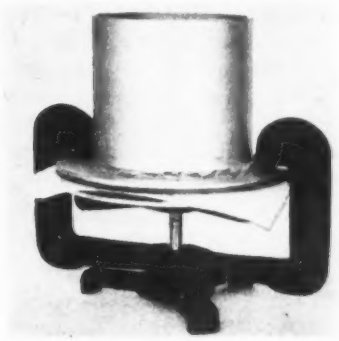
Equally, means for determining twist have been known for a long time. However, the Twist Tester shown in the subsequent picture has important improvements in that it has a take-up device which runs on 7 jewels and therefore friction is at a minimum. This makes possible the measurement of take-up in such enlarged form that precise determination can be made to one fortieth of an inch.



Twist Tester

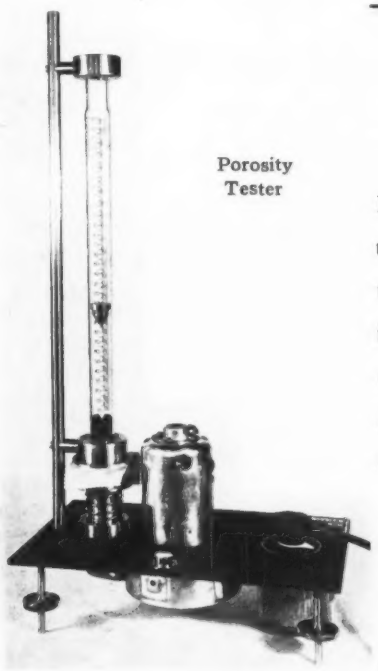
It is possible to determine more definitely the take-up of a yarn that is released after untwisting. If a yarn is over-stretched during spinning it can be proven by this instrument and thus dye streaks are traced to their true source. The direct indication of the number of turns upon the numerical counter with automatic digits is a further advantage, as is the S and Z setting for the direct indication of the direction of twist.

For testing the water-proofness of materials a simple and effective apparatus was constructed, which is shown in the following picture.



Waterproofing Tester

It consists essentially of a beaker of cast aluminum, the bottom of which consists of the material to be tested. This is held securely between rubber rings. Water is poured into this container and the time measured that it takes for penetration from one ring mark on the inside of the beaker to the next one. Another method consists of passing a measured quantity of water into this tester, to



Porosity Tester

NOTE: All halftones used with this article were furnished through courtesy of the *Rayon and Staple Fiber Handbook*.

let it stay for a given period of time, say 20 minutes, and thereafter to pour the water that remains in the container back into the graduated cylinder. The more porous the material tested, the less water can be returned in this manner. The advantage of this method lies in the fact that the material is tested under conditions that approximate practical actual usage, as in rain and showers.

Finally an instrument is shown for testing the porosity of a material.

In this apparatus a piece of fabric is inserted into a stream of air produced by a rotary fan blower, the speed of which can be adjusted by the rheostat at the right side of the picture. The stream of air lifts a float in the calibrated conical glass tube. The higher the float the greater the air penetration. In this manner it is possible to test the porosity of a fabric in an effective manner, easily understood by the average layman, without the use of auxiliary equipment such as stopwatches.

The above are a few only of the complete set of new methods and apparatus specifically developed to fill the requirements of mill, laboratory and purchaser, to determine significant physical factors of textile materials in a simple, correct and reliable manner.

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ONE HUNDRED AND SEVENTEENTH MEETING OF THE RESEARCH COMMITTEE

THE 117th meeting of the Research Committee followed the Council meeting in Boston on Friday morning, September 15, 1939. Present were Chairman Louis A. Olney presiding, W. D. Appel, K. H. Barnard, G. L. Baxter, J. R. Bonnar, W. H. Cady, H. Christison, F. Dannerth, C. Z. Draves, W. C. Durfee, A. Eavenson, D. Ferguson, A. H. Gaede, B. L. Hathorne, H. F. Herrmann, A. E. Hirst, A. P. Howes, E. H. Killheffer, G. R. Kremers, L. S. Lang, H. W. Leitch, A. R. Macormac, W. R. Moorhouse, G. A. Moran, A. Morrison, R. W. Philip, F. A. Prisley, B. A. Ryberg, W. M. Scott, C. A. Seibert, T. R. Smith, H. W. Stiegler, A. R. Thompson, Jr., H. S. Travis, B. Verity, W. S. Williams, P. J. Wood, W. H. Zillessen, and H. C. Chapin, Secretary.

Following a general report by the Chairman, there was further discussion of perspiration tests, in which it was agreed that there should be a second test, less rigorous than the present official test of the Association for fastness to perspiration; and that Mr. Ryberg should ascertain the desires of producers, merchants and the public with view to agreement on such a test. A photograph was shown of apparatus for conducting perspiration tests, designed by Mr. J. N. Dalton of Pacific Mills.

There was discussion as to whether development of washing fastness tests on dyed rayon should be undertaken. Mr. Prisley reported on a comparative investigation of methods for laboratory separation of wool and cotton instituted by A.S.T.M. Committee D-13, and Mr. Morrison and Mr. Ryberg added their comments on the work of our Association upon this problem. Mr. Barnard reported on progress of the research on textile finishes. Mr. Lang reported for Mr. Clayton, Chairman of the Committee on Shrinkage.

Respectfully submitted,

HAROLD C. CHAPIN, *Secretary.*

REPORT OF SYMPOSIUM ON COLOR TOLERANCE

A REPORT on the Symposium on Color Tolerance of the technical session of the 1939 annual meeting of the Inter-Society Color Council is now available. Copies of this report may be purchased by members of the A.A.T.C.C. as long as the supply lasts, at 50 cents each. Orders should be sent to: Inter-Society Color Council, P. O. Box 155, Benjamin Franklin Station, Washington, D. C.

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1914 VS. 1939

TO those of the textile fraternity whose span of activity includes the early period of the last World War, the contrast between the flurry currently being experienced in the dyestuff and chemical market and conditions as they existed upon the former occasion affords much food for thought.

It is true that we have with us on the present occasion a certain amount of war "jitters" founded in uninformed fear and without basis in fact. But this is as nothing to the absolute and well-justified panic which prevailed in 1914.

When war broke over an unprepared world 25 years ago, there was, to all intents and purposes, no such thing as an American dyestuff industry or, in fact, any dyestuff industry worthy of the name anywhere in the world outside of Germany and Switzerland. Because of the suddenness with which hostilities developed, there was no opportunity given for the accumulation of stocks in America from import sources and, within a very few months after the establishment of the German blockade, dyestuffs and other imported chemicals were selling at prices ten and twenty times above normal and, even at these exorbitant figures, supplies were practically unobtainable.

What a contrast exists today. Within the space of less than a quarter of a century America has developed a self-contained organic chemical industry second to none in the world. Despite a free flow of ocean borne commerce, American plants have been supplying, in recent years, well over 90 per cent of the tonnage of our domestic consumption of dyestuffs while, even in money value, the percentage approaches this figure. Moreover, because of the fact that the world has been upon the brink of war for more than two years, importing houses have had ample warning and have in all cases provided themselves with supplies of essential imports which, we are creditably informed, are sufficient to take care of ordinary domestic requirements for at least twelve months.

And, in addition to this most gratifying picture, we are advised by trustworthy sources that even those specialties which have heretofore been made solely abroad can be readily manufactured in this country. Hence there is little doubt that if the war develops into a protracted duel of endurance, domestic-manufactured products will be available for all necessary purposes before the accumulated supplies are exhausted.

This does not mean, however, that supplies of either domestic or foreign-made products presently on hand are sufficient to supply a false and speculative demand which has been stimulated partially by real, though uninformed, fear of shortage, but more particularly by the hope of being able to profit through an anticipated rise in prices.

Careful inquiries among all major suppliers of dyestuffs lead us to believe that there is no occasion for any regular customer to fear failure to receive from his usual sources of supply a normal quantity of dyestuffs and allied products at prices little, if any, above those prevailing during recent months. When, however, consumers multiply their demands and order, for immediate delivery, quantities vastly in access of their normal requirements, based on an average of recent months, they cannot reasonably expect to have these orders filled.

In other words, the position of the dyestuff manufacturers and importers is that they will take care of regular customers in accordance with a normal schedule, but that they cannot be expected to increase deliveries upon orders which are prompted either by fear or by the hope of making a trading profit.

The present status of our organic chemical manufacturing industry must be a source of tremendous satisfaction to those pioneers of 1914-18 who struggled so ceaselessly not only to establish the industry in this country, but to persuade Congress and the nation at large that its development was of sufficient importance to the welfare of the country to justify protection of an unusual sort.

Twenty-five years ago the public as a whole, and our legislators in particular, knew little or nothing of the key position in relation to all manufacturing industries occupied by organic chemistry. It needed a World War with the accompanying complete cessation of importations to prove to the man in the street that the great textile, paper, paint, rubber and countless other industries regarded as purely American were vitally vulnerable unless the sources of organic chemicals were equally self-contained.

Today the situation is reversed. Even the most poorly informed realize, partly through experience and partly through the instrumentality of the printed word, that of all key industries organic chemistry is the most fundamentally important.

Scarcely an industry exists today which does not depend at some vital point upon the fruits of organic chemistry. Many of our newer industries, such as synthetic fibers and plastics, are the creation, *in toto,* of the research chemist.

Let us give thanks, therefore, that our chemical pioneers of a generation ago were sufficiently farsighted to realize the importance of their work and that they were successful in selling to the American people and its representatives in Congress the vital necessity of the establishment of this industry as a self-contained American institution.

Let us never for one moment lose sight of the fact that this dearly won achievement of mind and industry is one of our most precious possessions. And let us never jeopardize its permanence by exposing it to ruinous competition from covetous competitor nations whose social standards are far below those with which we are blessed in this land of the free.

The Phthalocyanines

(Continued from page 610)

types: (*a*) the preparation of the pigment directly from phthalonitrile under certain catalytic conditions, and (*b*) preparation of various metal phthalocyanines followed by removal of the metal. The commercial processes in use at present are of the latter type. As is described in the literature and patents, the metal may be removed readily from many of the metal phthalocyanines. This is true particularly of magnesium phthalocyanine, lead phthalocyanine, stannous phthalocyanine, and disodium phthalocyanine. Usually treatment with acids is the simplest procedure, although it is known that the alkali metal phthalocyanines also are converted to metal-free phthalocyanine by the action of methanol.

Physical Conditioning. The statements previously made about conditioning copper phthalocyanine and its chlorinated derivatives apply also to the metal-free compound. Acid pasting may be used to secure the proper dispersion of the pigment. However, because of the ease of sulfonation, greater care must be observed in dissolving the pigment in sulfuric acid. Another desirable method of dispersing the pigment consists in demetallizing the alkali metal phthalocyanines with methanol. During the demetallization, the metal-free phthalocyanine is produced in a fine state of subdivision similar to that of the acid-pasted pigment. Choice of manufacturing processes depends upon cost and equipment considerations.

PROPERTIES AND USES OF METAL-FREE PHTHALOCYANINE

Metal-free phthalocyanine is similar in physical appearance to copper phthalocyanine except that it is greenish blue in the dispersed form. It has the same insolubility in organic solvents and solubility in strong acids as the pigments already discussed. Likewise, it has the stability to heat, acids, alkalies, and oxidizing and reducing agents that is typical of the other pigments of this series. To the user, the importance of the pigment other than its fastness properties is the fact that it is a brilliant greenish blue (peacock blue) of high tinctorial value and purity of shade. Its shade can be approximated by mixing copper phthalocyanine with chlorinated copper phthalocyanine, but the shade of the mixture is somewhat duller.

This pigment has been available to the pigment trade for only a few months; but it is apparent that it will be an important product, although to a lesser degree than the blue and green discussed above. It will be used in printing inks where brilliant greenish-blue shades are desirable; in paper coloring, especially for wrappings for food products where the presence of copper is objectionable; in the wallpaper trade where brilliant greenish-blue shades are in demand; and perhaps in the rubber trade where there is an aversion to colors containing copper.

Since metal-free phthalocyanine is intermediate in shade between the blue copper phthalocyanine and the green chlorinated copper phthalocyanine, the expectation is that it will find its major use where the presence of copper is undesirable or where the slight advantage in brilliance over mixtures of the blue and green is important. Nevertheless, unexpected differences in properties appear without warning in pigment applications, and it is possible that other important uses for this color will result because of some physical differences not yet recognized.

SULFONATED COPPER PHTHALOCYANINE

The first interest in the phthalocyanine series was the use of these products as pigments. It was logical, however, that when this brilliant blue chromophore became available, every possible effort would be exerted to utilize the structure in soluble dyes for textile and other dyeing purposes. Of the many soluble phthalocyanines prepared, the only type which has found commercial application to date is sulfonated copper phthalocyanine.

Preparation. The phthalocyanine molecule responds readily to the usual sulfonation conditions, and it is possible to introduce sulfonic acid groups in any or all of the four benzene nuclei of copper phthalocyanine. As might be expected, the solubility in water, particularly as alkali metal salts, of the sulfonic acids increases as the degree of sulfonation is increased. For most purposes, however, the disulfonic acid is the most suitable product.

Properties. Sulfonated copper phthalocyanine in aqueous solution is a brilliant greenish-blue dye of moderate solubility. It shows some affinity for various textile fibers but cannot be classed as a highly substantive dye. In the soluble form the color has only moderate fastness properties; it is quite inferior to the insoluble pigment although it compares favorably with soluble colors of comparable shade and brilliance. The sulfonation products may be

converted readily to insoluble pigment lakes and toners, the alkaline earth salts being quite insoluble and readily extended on the usual white pigment bases. In the form of its lakes and toners, the sulfonated product has excellent fastness properties which approach those of copper phthalocyanine itself. Sulfonated copper phthalocyanine also can be converted to salts with organic bases, such as long-chain amines, and thus yield brilliant bluish greens which are soluble in various organic solvents, particularly in alcohols.

Uses. The soluble salts of sulfonated copper phthalocyanine find some use in direct and mordant dyeing of cotton, in dyeing of animal fibers, and especially in mixtures as dyes for union textiles. The fastness properties of the colors are of the same order as those of the acid colors previously available, but the brilliance of shade has been found superior in most cases to the products previously used. Since the colors have relatively low affinity for the various fibers, the washing fastness of fabrics dyed with these products is not of a high order.

The amine salts of sulfonated copper phthalocyanine find application in spirit inks, stains, and similar coloring compositions. These new products provide a combination of brilliance of shade and fastness properties hitherto unavailable in this field.

The toners and lakes prepared from sulfonated copper phthalocyanine are finding application in the usual pigment fields, such as in printing inks and various coating compositions. As yet, the relative merits of these products and the insoluble phthalocyanines have not been demonstrated conclusively, and it is difficult to state the probable importance of these lakes and toners. Perhaps the fact that they show little bronzing in deep shades will result in their adoption in various finishes in preference to copper phthalocyanine itself. However, it can be said that these products also have the brilliance of shade and excellent fastness properties of the insoluble color pigments of the phthalocyanine series.

ACKNOWLEDGMENT

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TRADE NOTES • NEW PRODUCTS

• AMERICA'S CHEMICALS

America's self-sufficiency in dyestuffs and other textile chemicals is assured regardless of foreign developments, asserted Ansco G. Bruinier, Jr., of the du Pont Company Dyestuffs Division, in an address on September 18th before the Virginia State Association of Dyers and Cleaners, according to a recent news release of the du Pont Co.

"The chaotic conditions existing abroad," said Mr. Bruinier, "bring to mind the desperate position in which textile manufacturers and others found themselves only twenty-two years ago when importations of dyes from Europe came to a standstill. Today, however, American consumers of dyes no longer need worry, as the range of dyes manufactured here is sufficiently broad to take care of all coloring needs.

"During the World War, before the United States became involved, the need for a self-contained American dyestuffs industry became evident, and it was through the courage and faith of far-seeing industrial leaders that a new American industry was born. The du Pont Company was among those who pioneered in this complex field, particularly in the development of fast vat colors. The courage and faith of these industrial pioneers was well rewarded, since today the American dyestuffs industry is second to none."

Mr. Bruinier also spoke of the trend in recent years toward synthetic textile fibers. "The development," he said, "of multi-fiber fabrics taxes to the utmost the ingenuity of both the dyestuff manufacturer and the textile processor. The successful dyeing of a fabric made from several different kinds of fibers may call not only for new application methods, but also for new types of dyestuffs.

"In addition to synthetic dyestuffs, the chemist has created many other products which are used by the textile industry. Examples include the new 'soapless soaps' which work equally as well in hard water as in soft water, saving textile finishers thousands of dollars formerly spent on wasted soap, damaged goods, and for softening water; the new 'Zelan' finish for fabrics which imparts a softness and water repellency highly resistant to both drycleaning and laundering; and other products such as delusterants, mildew-preventives and crush-resistant finishes, which not only protect but enhance the appearance of finished fabrics.

"There is an increasing demand on the part of the consumer and processor for greater fastness in colored fabrics. This demand is being satisfactorily met by American dyes today. While there are certain types of fibers and fabrics, which, because of their chemical construction, cannot be processed with absolutely fast colors, research is constantly in progress to overcome these deficiencies.

"The American dyestuffs industry is regarded as a key industry. Not only does it provide color for many materials, but its continuous research also produces for physicians and hospitals countless new developments in the pharmaceutical and medical fields."

• STUDY OF DISTRIBUTION COSTS

Release of one of the most complete studies of distribution cost accounting ever published was announced by the Department of Commerce recently.

The handbook, prepared in the Distribution Cost Section of the Bureau of Foreign and Domestic Commerce by H. F. Taggart, special consultant, contains material of value to all businessmen.

Of particular value is the information explaining how business records may be analyzed to determine the cost of each merchandising department, each commodity, each customer group, and each territory of sales operations. All methods of cost allocations and expense breakdowns used in the handbook have been tested and found satisfactory either by the Department of Commerce or by trade associations and accountants of national recognition.

While the subject of cost accounting is necessarily technical, the handbook is supplemented with detailed explanations and numerous illustrations.

Commerce Department experts point out that the manual should be helpful to all merchants in guiding their efforts to produce greater profits through more adequate planning and budgetry control. Particularly close scrutiny has been made of every service and every business function performed, with its attendant cost to the businessmen and therefore to the ultimate consumer.

Special emphasis is laid on distribution cost accounting problems confronting wholesalers. However, the basic nature of the material makes it of value to all businessmen, whatever their interest may be.

Copies of this manual, "Distribution Cost Accounting for Wholesaling," further identified as Domestic Commerce Series No. 106, can be obtained for 15 cents a copy from the Government Printing Office, Washington, D. C., or any district office of the Bureau of Foreign and Domestic Commerce, located in principal cities throughout the country.

• REGISTRATION, LOWELL TEXTILE INSTITUTE

Registration at Lowell Textile Institute this fall totaled 299, with a freshman class of 105. The registration is the largest in the history of the school. Changes in the instructing staff of the textile chemistry and dyeing department include the promotion of John H. Skinkle, instructor for the past 13 years, to assistant professor and the appointment of Dr. Paul C. Panagiotakos as instructor in organic chemistry. Mr. Skinkle is well known to the readers of the REPORTER as the author of the series of articles on textile testing which is to be brought out in book form shortly.

• CIBA REVIEW

Copies of *Ciba Review*, Number 25, September, 1939, have recently been distributed. Featured in this issue is the subject: "Paris Fashion Artists of the Eighteenth Century." Contents are described by the following titles: The Rise of the French Fashion Artist; The Fashion Artist at Work; Topical Fashions; Great Paris Fashion Artists; 18th Century Milliner's Terms; Historical Gleanings. This issue is replete with illustrations carrying out the theme.

• ROHM & HAAS RELEASE

Rohm & Haas Co., Inc., 222 West Washington Square, Philadelphia, Pa., has recently issued a leaflet describing the following new product:—

RHotex A-20—a new synthetic gum which is the sodium salt of a polymerized resin acid in an aqueous solution. The product is said to be outstanding for its unusually high viscosity and its complete solubility in water. While readily miscible with acid, alkali, or salt solutions it is not miscible with organic solvents. It is stated that when it is deposited from an aqueous solution it has excellent film forming qualities. Furthermore, it has good emulsifying and dispersing properties. The manufacturers recommend its use wherever natural gums such as tragacanth, karaya and locust bean are employed. It is stated that RHotex A-20 can be used as a water soluble thickener, a clear, colorless film base, a solvent resistant coating, a printing paste thickener, a warp sizing agent, an emulsifying and dispersing agent and an adhesive compound.

Copies of the leaflet, which gives complete details regarding the product, are available upon request.

• PHOENIX RELEASES

Phoenix Color & Chemical Co., 24 Van Houten Street, Paterson, N. J., announces release of two new colors:—

Paraphen Brown R; Paraphen Brown V —two improved direct colors for cotton, rayon, etc., which give brown shades said to be fast to washing and light when aftertreated on the fiber with diazotized paranitraniline. They are recommended by the manufacturers for beam or package dyeing.

• WILLIAM WILLHEIM PLANT AT AUCTION

The entire machinery and equipment of William Willheim Co., Inc., printers, dyers and finishers of textile products, 222 Passaic Street, Passaic, N. J., will be sold at auction on Tuesday, October 24th, at the plant in Passaic.

The Willheim Company has been well regarded in the textile industry for thirty years. It is reported that the company maintained a large and complete plant capable of handling 2,000 pieces per day. The sale includes twelve 6-, 8- and 12-color print machines, dryers, tentering frames, palmers, quetsches, extractors, decating machines, calenders, motors, 600,000 lbs. copper print rolls, machine shop equipment, chemicals and varied factory equipment. Much of the machinery is individually motor driven. The plant was in operation up until July of this year.

The auction sale has been ordered by Harry B. Haines of Paterson, the trustee in bankruptcy, and will be under the management of Samuel T. Freeman Co., auctioneers. The trustee stated that every item will be sold to the highest bidder and is subject to the confirmation of the Court.

• 1914 AND THE PRESENT

In common with other manufacturers of ...estuffs and related chemicals, The Calco ...hemical Company, Inc., Bound Brook, ...J., a Division of American Cyanamid ...ompany, reports in a news release a ...ecent rush of orders reminiscent of the ...xciting days of 1914 and 1915. This they ...iew as a symptom of "war jitters" which ... unjustified in the light of today's con...itions. They are employing both special ...ulletins and paid advertising to emphasize ...he vast difference between the situation ...hen and now as regards the ability of ...merican manufacturers to supply the ...ountry's full requirements for dyes and ...hemicals.

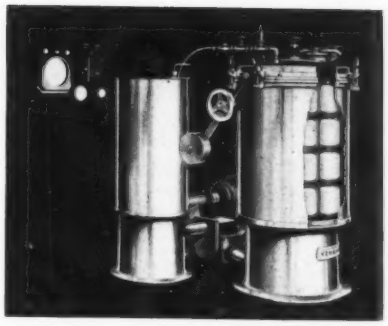
In 1914, it is recalled, approximately 90 ...er cent of the country's requirements were ...upplied by foreign sources. Since then, ...hey claim, Calco has grown from an in...ignificant standing start to the point where ...hey are now one of the country's largest ...roducers of dyes, intermediates and re...ated chemicals. Their production has not ...nly increased tremendously in volume, but ...as become impressively diversified as well. ...hey add that the progress of many other ...omestic companies has paralleled that ...f Calco, bringing present normal capacity ...o well over 90 per cent of the country's ...ntire needs.

From this they reason that there is every ...ikelihood that American firms can supply ...irtually every domestic requirement for ...yes and chemicals—not only in quantity ...ut in quality as well. They are therefore ...rging that orders be kept in pace with ...ctual needs—both as a means of minimiz...ng the spread of "war jitters"—and as an ...id in keeping manufacturing schedules at ...fficient, economical levels. They add a ...rther assurance that not only do they see ...o danger of a general shortage similar to ...hat of 1914, but that they are taking every ...eans to assure users of protection in ...eeping prices within reasonable levels.

In the event that unforeseen circum...tances make such a course necessary, they ...ndicate that preference in the filling of ...rders will be accorded to present custom...rs.

• NEW VENANGO MACHINE

Venango Engineering Company, Phila...elphia, builders of textile dyeing equip...ent, has entered the package yarn field ...ith a new dyeing machine for which is ...laimed important improvement over pre...eding types of equipment for the purpose. ...utstanding among the new features of ...his machine is a pneumatic 4-way control ...ransfer valve which is described as revolu...ionary in its benefits. This valve per...orms the important function of changing ...he direction of dye liquor flow through ...he packages at timed intervals regularly ...epeated throughout the process. It is an



New Venango Pneumatic Package Yarn Dyeing Machine, showing, in lower center, the simple and compact pneumatic 4-way control transfer valve that is one of the distinctive features of this machine.

accepted fact that uniform dyeing depends to a large extent on the regularity of these timed changes of dye flow. With the new Venango pneumatic type automatic valve, it is claimed, these changes are effected with increased speed and accuracy of timing, giving a positive control of uniform dyeing. An increased efficiency of dye flow through the packages is claimed because, by this method, pressure is transferred instantly and maintained without variation in either direction, and without appreciable lag between changes in flow. Further advantages of the Venango valve are claimed in its extreme simplicity of design, in which limit switches, speed reducers, gears, levers and other familiar accessory mechanism of other type valves are eliminated along with intricate electrical connections. The valve is exceedingly compact, reducing space requirements for the complete assembly of dye tank and accessories.

Another feature of unique advantage is the design of the dye tank cover, or lid. In this design, all overhead weights and all struts and braces are eliminated. As the lid is raised from cover position, it swings outward and downward on a balanced hinge to a resting position at which a considerable portion of the lid is below the rim of the tank. Thus the lid requires the minimum of head room and is kept well out of the way of the operators in loading and unloading the machine. Raising or lowering the lid is accomplished by simply turning a hand wheel at either side of the tank.

Constructed throughout of stainless steel, the Venango pneumatic package dyeing machine is built in a variety of sizes for all required capacities. Complete description may be had by writing Venango Engineering Company, Philadelphia, for the attractive new folder they have just issued on this machine.

• COMMERCIAL PRODUCTION OF TEXTONE

According to a recent announcement from The Mathieson Alkali Works, Inc., reports from dyeing and finishing plants now operating the new Textone process have proven so favorable that plans have been completed and work started on the first commercial unit for the production of the new chemical. It is stated that the plant will be in production before the end of the year.

The new plant represents the culmination of five years of study in Mathieson's research laboratories for a practicable, commercial process for making sodium chlorite ($NaClO_2$), one of the essential ingredients of Textone. Sodium chlorite has, of course, long been known as a chemical compound, but it has remained for Mathieson to see the possibilities of this chemical and to develop the first commercial process of manufacture. The process is a complex and unusual one; however, Mathieson claims to have ironed out all the kinks in the process and definitely established its practicability for large scale production.

The Textone output of the present pilot plant is currently being used by a few prominent New England plants in single-operation scouring and bleaching processes, and as an adjunct to existing kier processes and by a number of other plants for experimental work pending the completion of the new commercial unit.

• SYMPOSIUM ON TEMPERATURE

A symposium on temperature will be held in New York City at the Pennsylvania Hotel, November 2 to 4, 1939, by the American Institute of Physics, 175 Fifth Avenue, New York, with the cooperation of the National Bureau of Standards, the National Research Council, and officers and committees of many technical societies.

The program is in charge of representative committees of authorities in various fields, who have arranged for a program of 100 or more papers on scientific and technical subjects, which will be presented in concurrent sessions of selected groups. All interested persons active in science or engineering are cordially invited to attend the sessions, and take part in the discussions of papers. A complete program containing full abstracts of the papers to be presented will be mailed in advance on request to the Institute. It is suggested that those who expect to attend will inform the Institute and make their hotel reservations early. There will be a registration fee of $1.00. The Chairmen of the committees are Gustav Egloff, A. W. Ewell, C. O. Fairchild, J. D. Hardy, H. F. Mullikin, F. H. Norton, R. B. Sosman, C. B. Veal, H. T. Wensel, and C. B. Wilkes. H. A. Barton, Director of the Institute, is Chairman of the Main Committee.

• JOINS REICHHOLD CHEMICALS, INC.

Dr. C. A. Knauss joined the Reichhold sales organization on September 15th and is now devoting his efforts to the sale and servicing of RCI products in the Metropolitan New York district.

Dr. Knauss had his first experience on problems appertaining to the proper formulation of paint products while at Lehigh University, where, in association with Dr. J. S. Long, he participated in extensive research work on linseed oil. Upon completion of his schooling, Dr. Knauss became affiliated with Dr. Gardner's staff at the Institute of Paint & Varnish Research in Washington, later serving as technical director for John Lucas & Company.

For the past five and one-half years, Dr. Knauss served as vice president in charge of sales for Nuodex Products, Inc., during which time he contacted most of the paint and varnish manufacturers in the United States and Canada and addressed all the paint and varnish production clubs.

Incidentally, Dr. Knauss is available for production club talks, arrangements for which can be made by addressing Reichhold headquarters at Detroit, 601 Woodward Heights Boulevard.

• PURCHASES PUMP CO.

Announcement has been made by the Food Machinery Corporation, from their Los Angeles offices, of the purchase of Kimball-Krogh Pump Company, a Division of the Victor Equipment Company.

The Food Machinery Corporation are large manufacturers of deep well pumping equipment through their Peerless Pump Division and Kimball-Krogh will now be merged into another pump manufacturing unit of the Food Machinery Corporation.

Vernon Edler, Vice-President of Food Machinery Corporation, handling the negotiations for his company, stated that the merger will enable Food Machinery Corporation to offer an entirely new line of pumps in addition to the regular Peerless line which comprises the Peerless turbine pump for deep wells, the Peerless propeller pump for drainage and flood control, and the Peerless Hi-Lift pump for domestic and small capacity deep wells. The lines to be offered through their new division will include Kimball-Krogh's newly developed sewerage disposal pump, a special horizontal centrifugal pump and others.

Los Angeles being the largest turbine pump manufacturing center, the main office of Food Machinery Corporation's pump manufacturing divisions will remain at its present quarters, but through their four pump factories and numerous factory branches, Food Machinery Corporation will continue to increase their facilities for serving the agricultural, municipal and industrial trade throughout the world.

• CIBA RELEASES

The following publications have been issued by the Ciba Company, Inc., representing the Society of Chemical Industry in Basle, announcing new products and processes.

Neocotone Orange GR—this is another new member of the Neocotone series. The advantages of Neocotone Orange GR, as with the other Neocotones are said to be good solubility in water, simple method of preparation of the print paste, unlimited stability of the paste, fixation in regular ager, possibility of combination with vat dyes, chrome colors and also aniline black and the facility of mixing the Neocotones to make composite shades. As with the other types, this new product is especially recommended by the manufacturers for direct printing of cotton and rayon, also for padding, whereby white or colored resists and white and colored discharges are possible. Fixation is accomplished by a short pass in an ordinary ager, followed by a pass through a weak alkaline bath. Circular No. 513.

Direct Dyestuffs on Cotton Pieces—this card shows by means of 118 dyeings, the direct dyeing and after-treated dyestuffs. The card contains all available dyeing processes, alkaline, neutral and acid dyebaths, topping with basic dyes, after-treatment with metallic salts, formaldehyde and with Lyofix DE and Sapamine KW. The fastness properties are arranged in tabular form near the dyeings. Sample card No. 1675.

Rosanthrene and Diazo Fast Colors on Cotton Yarn and Cotton Pieces. These dyes are applied in an alkaline Glauber's salt bath, then diazotized and developed in the regular manner. In contrast to the former card No. 1217, the following new types have been added: Rosanthrene Orange 2R, Diazo Brilliant Green G and Diazo Fast Blue 4BW. The fastness properties are arranged in tabular form near the dyeings. Sample Cards Nos. 1690 and 1691.

Quantitative Microscopical Analysis of Mixed Fabrics*

HAZEL M. FLETCHER**

ALTHOUGH there is an increasing realization that the volume of each fiber present in a mixed fabric is as important as the weight of each fiber present, comparatively little work has been done on quantitative microscopical analysis. Heretofore, most quantitative analyses of fibers have been based on percentage weight as determined by chemical analysis. The microscope is adaptable to volumetric as well as to gravimetric determinations. Quantitative microscopical analysis of textile fabrics is sometimes the only method which can be used. Fabrics made of yarns which are blends of fibers lend themselves to microscopical analysis. If one kind of fiber constitutes a very small percentage, it is often better to resort to microscopical analysis rather

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**Kansas Agricultural Experiment Station.

than to a chemical analysis in which the loss of the fiber of small percentage may amount to considerable. It should be noted however that in general microscopical analysis is only accurate enough when samples are too small for chemical analysis, or, when chemical methods will not differentiate; e.g., wool and mohair, cotton and linen.

Blends of viscose rayon and linen, or of viscose rayon and cotton, may be analyzed by dissolving the rayon in calcium thiocyanate. After the solution is used it must be diluted until the rayon is precipitated, and then evaporated before it is ready to be used again. This method is long and tedious, and the microscopical analysis is preferred to the chemical analysis.

Blends of different kinds of wools cannot be separated by chemical analysis, and microscopical methods must be used. Skinkle[3, 4] and von Bergen[6] have done analyses of wool and mohair and other animal fibers, identifying the kind of fiber by measuring scale sizes and diameters and counting the number of each bind.

Heerman and Herzog[1] showed that the percentage of each kind of fiber in a mixture could be found by the equation

$$\text{Percentage of fiber A} = \frac{100\ n_a g_a}{n_a g_a + n_b g_b}$$

where n is the number of fibers and g is the weight of each fiber per unit of length. Skinkle[4] in his work on animal fibers which are nearly round in cross section and of approximately the same density has expressed the percentage by the equation

$$\text{Percentage of fiber A} = \frac{100\ n_a d^2_a}{n_a d^2_a + n_b d^2_a}$$

where d is the average diameter of the fibers and n is the number of fibers.

This equation can be modified to calculate the percentage of fibers which are of irregular cross section, without the determination of weight of the fibers per unit length as done by Heermann and Herzog[1].

In this investigation two methods were used for counting the number of each kind of fiber. For blends of linen and viscose rayon, of cotton and viscose rayon, or of cotton and linen, the number of each kind of fiber was counted by cutting as small a length of the yarn as possible, less than one-sixteenth of an inch, with small shears. The small lengths were mounted in glycerine and teased out as uniformly as possible on the slide. A magnification of 100 or less was used with a 16-mm. objective, and the total number of fibers of each on the entire slide was counted by moving the slide with a mechanical stage which had two graduated scales at right angles. The distinguishing of linen from cotton could often be facilitated by placing the slide between crossed Nicol prisms. Ten slides or more were prepared from yarns taken from various parts of the fabric, and the average of the counts on the ten slides was taken as the number of fibers of each kind in the yarn.

The above method was used for blends in which one kind of fiber made up a small percentage of the yarn and for fibers for which it is difficult to make cross sections.

For blends of different kinds of wools, of rayon and wool, and of wool and cotton, the counting of the fibers was done by making cross sections by the Viviani cork method.

A magnification of about 300 with a 4-mm. objective was used. A field was chosen at random, and the number

Fig. 1—Blend of wool and cotton. Cross-section; Glycerine mount.

X380

Fig. 2—Blend of wool, delustered viscose and dyed viscose. Cross-section; Glycerine mount.

X380

Fig. 3—Blend of wool, silk and rabbit fur. Cross-section; Glycerine Mount.

X380

of sections of each kind of fiber was counted. Ten to twenty different fields of the same size were counted, and the average of each kind was taken as the number of fibers. Figures 1, 2 and 3 show photomicrographs of cross sections of yarns of various kinds of mixed fabrics.

The relative areas of the fibers were found by drawing 10 or more cross sections with the camera lucida as pointed out by Preston[2]. The cross sections were cut out and weighed on an analytical balance, and the average weight of the paper drawings of each kind of fiber was calculated and taken as proportional to the size of the fiber. The percentage by volume of each fiber in a blend can be expressed by the equation

$$\text{Percentage of fiber A} = \frac{100\ n_a w_a}{n_a w_a + n_b w_b}$$

The percentage by weight of each can be expressed by the equation

$$\text{Percentage of fiber A} = \frac{100\ n_a w_a g_a}{n_a w_a g_a + n_b w_b g_b}$$

In the equations n is the number of fibers, w is the average weight of camera-lucida drawings of the cross sections, and g is the specific gravity of the fiber. The values of the specific gravities were taken from Heermann and Herzog[1] and the International Critical Tables[5].

Table 1 shows some results of analyses of blends of mixed fabrics made by the author and her students. Microscopical analyses were compared with those obtained by chemical analyses. In the chemical analyses $AlCl_3$ was used to carbonize the viscose rayon and cotton, and Lowe's reagent to dissolve the silk. A preliminary study of the chemical methods showed the error in each method to be less than one per cent. It will be noted that the differences by chemical and microscopical analyses are small, the greatest error occurs when cotton is one of the constituents.

TABLE 1

Results of Microscopical Analyses by Weight of Blends of Mixed Fabrics Showing Comparison with Chemical Analyses

Fabric No.	*Chemical analysis*	*Microscopical analysis (by weight)*
1 Alpaca	53% Viscose rayon 47% Wool Viscose carbonized with $AlCl_3$ (by Hollis)	55% Viscose rayon 45% Wool (by Floersch)
2 Flannel	51% Wool 49% Cotton Cotton carbonized with $AlCl_3$ (by Hollis)	56% Wool 44% Cotton (by Zink)
3 Flannel	65% Viscose rayon 35% Wool Viscose carbonized with $AlCl_3$ (by Fletcher)	65% Viscose rayon 35% Wool (by Floersch)
4 Granite Cloth	52% Viscose rayon 48% Wool Viscose carbonized with $AlCl_3$ (by Hollis)	56% Viscose rayon 44% Wool (by Zink)
		54% Viscose rayon 46% Wool (by Floersch)
5 Novelty granite cloth	58% Viscose rayon 42% Wool Viscose carbonized with $AlCl_3$ (by Fletcher)	58% Viscose rayon 42% Wool (by Dennhardt)
6 Novelty knit dress fabric	58% Silk 42% Wool and rabbit fur Silk dissolved in Lowe's reagent (by Dennhardt)	58% Silk 36% Wool 6% Rabbit fur (by Dennhardt)
7 Printed dress fabric		71% Viscose rayon 29% Linen (by Zink)
		68% Viscose rayon 32% Linen (by Dennhardt)
8 Novelty mixture		83% Wool 17% Rabbit fur (by Fletcher)
9 Novelty mixture		85% Wool 15% Rabbit fur (by Fletcher)

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• CLASSIFIED ADVERTISEMENTS •

POSITION WANTED: SALESMAN AND DEMONSTRATOR—6 years' experience in the finishing of cotton and rayon mixtures. Acquainted with New England territory. Write Box No. 215, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

POSITION WANTED: Textile Chemist with 17 years' experience in cotton, rayon, silk finishing and printing, dyestuff and organic research, desires permanent position in operating or technical sales. Broad operating and development experience; anti-crease, flameproofing, permanent, pre-shrinking, water-repellent, and various resin finishes. Understands costing. Cooperative ability. University and post-graduate training. Write Box No. 216, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.